Polynomial method for canonical calculations

N.K. Kuzmenko [a,*], V.M. Mikhajlov [b]

[a] *V.G.Khlopin Radium Institute, 194021 St.-Petersburg, Russia*
[b] *Institute of Physics St.–Petersburg State University 198904, Russia*

Abstract

A practical version of the polynomial canonical formalism is developed for normal mesoscopic systems consisting of N independent electrons. Drastic simplification of calculations is attained by means of proper ordering excited states of the system. In consequence the exact canonical partition function can be represented as a series in which the first term corresponds to the ground state whereas successive groups of terms belong to many particle-hole excitations (one particle-hole two particle-hole and so on). At small temperatures ($T < 10$ inter-level spacings near the Fermi level) the number of terms which should be taken into account is weakly dependent on N and remains < 10 even if $N \sim 10^5$. The elaborated method makes canonical calculations to be not more complicated than the grand canonical ones and is free from any limitations on N and T.

Key words: Canonical vs grand canonical calculations, Mesoscopic systems.
PACS: 05.30.Fk, 02.10.Ox

* Corresponding author.
 Email address: `Kuzmenko@NK9433.spb.edu` (N.K. Kuzmenko).

1 Introduction

The characteristic feature of the modern stage in studying mesoscopic systems is a possibility to fix individual properties of investigated objects such as chemical composition, size geometric shape and particle number. The well known example of such investigations is the discovery of electronic shells in alkali metal clusters [1]. The other branch of researches is connected with recent advances in the development of new techniques for fabricating two- or three-dimensional micro- and nano-structures that enables current experiments to investigate variations of both the exact number of electrons on such mesoscopic structures and their geometrical shapes with a precise control in all dimensions. Frequently experiments are produced so that investigated systems may exchange energy with surroundings (they are embedded in heat reservoir), i.e. they are kept at an invariable temperature, however the exchange by particle is absent. Thus, such systems constitute a canonical ensemble, and the most appropriate theoretical method for their statistical description is the canonical formalism.

The papers of Denton, Mühlschlegel and Scalapino [2] were the first where the canonical description was developed in applying to electrons in small metallic grains. At that time it was impossible to fix the shape and particle number of each grain. Therefore for constructing the canonical partition function Denton et al made the simplest assumption that the energy spectrum of free electrons in a metallic grain is equidistant (the equal level spacing model) and two-fold degenerated if there is no magnetic field. Using reasonable approximations ($M > N \gg 1$, M is number of single electron levels) Denton et al established an analytical expression for the canonical partition function. They showed that the main differences between the canonical and grand canonical values of the heat capacity (C) and magnetic susceptibility (χ) lie at small temperatures $T < \delta$ (δ is the mean level spacing). Besides they found that at $T \gg \delta$ the grand canonical heat capacity exceeds the canonical one by $k_B/2$ (k_B is the Boltzmann constant). The partition function of Denton et al takes into account energy variations in an applied uniform magnetic field. They manifest themselves in oscillations of χ and C with growth of the field. Such oscillations are typical for charged particle systems [3] however the strong periodicity in the oscillations is a feature of the equal level spacing.

It is worthwhile emphasizing the N-independence of thermodynamic quantities as functions of T/δ in the canonical calculations of Denton et al at $M > N$, $M, N \gg 1$. It is caused by a relatively narrow layer of single particle levels near the Fermi energy, which mainly contributes to the partition function, and by the identical for any N structure of the single-particle energy spectrum in this layer.

The canonical formalism was also used by Brack, Genzken and Hansen [4] for calculations of thermal properties of the valence electrons in alkali metal clusters. In this case free electron energy spectra contain considerable gaps that accounts for enhanced stability of clusters with the magic numbers of atoms. Brack et al showed that the shell structure reveals itself in the theoretical heat capacity. However, the difference between the canonical and grand canonical shell effects is quite noticeable only at temperatures which are less than or of the same order as the mean level spacing δ_F near the Fermi. Thus, both investigations, [2,4], point out the region of the temperatures, $T < \delta_F$, where the comparison of the canonical and grand canonical calculations is of the most interest. Besides, in the center of attention should be magic electron numbers (if they appear in the system) since the existence of such N is a consequence of the appearance of an energy gap near the Fermi level that enhances the difference between canonical and grand canonical results. It is well known that $T < \delta_F$ is the best regime for observing size effects in mesoscopic systems [5,6]. Therefore the canonical approach at these temperatures can give more precise theoretical information than the grand canonical calculations.

In order to calculate the partition function $Z(N, M)$, occupation numbers, internal energy and other thermodynamic quantities Brack et al used recurrence relations connecting $Z(N, M)$ with those for smaller N and M. Following this procedure they found that $N(M - N)$ calculation steps were needed to obtain the final result, i.e. for $M > N \sim 10^2$ ($N(M - N) \sim 10^4$). Such method is still manageable for N up to a few hundreds, however it could be hardly applied to N and $M > 10^3$. Thus the constructing of the effectively working canonical formalism without restrictions on the particle number and applicable to arbitrary spacing distributions is a problem that has to be solved.

Parallel with the exact canonical calculations in Ref. [2,4] approximate methods have been suggested for constructing the canonical partition function of the normal (nonsuperconducting) systems. One of them Ref. [7] replaces the projection integral over the gauge variable φ ($0 \le \varphi \le 2\pi$) by the discrete sum that involves L terms. These terms depend on $2\pi l/L$ (instead of φ) where the integer l varies from 0 to $L - 1$. As shown in Sec.1 this method can be viewed as the partial projection. It is the more precise the higher is the value of L. In Ref. [8] this method was employed by Frauendorf and Pashkevich to calculate sodium cluster shape and free energies. Another method suggested by Rossignoli consists in the evaluation of projection integral in the saddle-point approximation. Such approach turns out to be quite satisfactory in the case of not very small temperatures and particle numbers as was demonstrated by calculations of nuclear level densities in Ref. [9].

Our effective version of the canonical approach is based on the polynomial representation of the partition function. Last years such representation is discussed in the literature [10,11], however our practical version of polynomial

calculations was elaborated many years ago for a projection method applied to the Bardin-Cooper-Schriffer (BCS) function for describing the particle number conserving pairing correlations in nuclei [12].

There is an obvious analogy between the BCS function and grand canonical partition function for the independent electron model (IEM). Both can be represented as products $\prod(1 + f_s)$, where f_s for the BCS function is $(v_s/u_s)a_s^+a_{\bar{s}}^+$ (v_s, u_s are the Bogolubov parameters, $a_s^+a_{\bar{s}}^+$ is the operator of the fermion pair creation in time conjugated states s and $\bar{s}$) while for the canonical partition function f_s is $\exp(\varepsilon_s - \lambda)/kT$, ε_s and λ being the energy of a single -particle state s and the chemical potential respectively. After projection onto a fixed particle number N both functions gain the form of a N-th order symmetric polynomial $[N]$. This polynomial $[N]$ consists of $M!/N!(M-N)!$ terms (as before M is the total amount of employed single-particle states) and each term in it is the production of N different f_s, i.e. $[N]$ includes all distributions of N BCS pairs or N electrons over M states. For large M and N the total number of terms in N may be enormous, however a hierarchy of terms can be established according to their surviving at $G \to 0$ (G is the pairing strength) or $T \to 0$. The first term of this hierarchy corresponds to the independent fermion ground state in which all single-particle states are occupied up to ε_F. The second group of terms corresponds to simplest excitations: in the BCS theory it is a particle pair $a_s^+a_{\bar{s}}^+$ above ε_F and a hole pair $a_s a_{\bar{s}}$ beneath ε_F, for free electrons in a cluster it is one particle-hole excitations. The third group of terms corresponds to a shift of two BCS particle pairs or two cluster electrons above ε_F. This alignment of many particle-hole excitations continues till all pairs or cluster electrons are lifted above ε_F.

The common property of the projected BCS and the canonical partition functions is mutual independence of probabilities of particle and hole excitations. This probability depends only on the energy of the single-particle level on which a BCS fermion pair or a cluster electron is located. For the BCS case it is (v_s/u_s) for levels with $\varepsilon_s > \varepsilon_F$ while for levels with $\varepsilon_s \leq \varepsilon_F$ it is (u_s/v_s) , for cluster electrons it is $\exp(\lambda - \varepsilon_s/kT$ if $\varepsilon_s > \varepsilon_F$, or $\exp(\varepsilon_s - \lambda)/kT$ if $\varepsilon_s \leq \varepsilon_F$. Thus summing over particle and hole excitations can be performed independently. The contribution of each group of n-particle excitations to $[N]$ includes a sum running distributions of n electrons (here we mean cluster electrons) over particle levels (with energies above ε_F). These sums can be also represented as symmetric polynomials, now they are of n-th order ($n < N$). Analogous polynomials arise for hole excitations, but in this case electrons are distributed over hole levels (below and including ε_F). Though the convergence of appearing series is absolute its rate is determined by T/δ_F. Practically for $T/\delta_F < 1$ they include not more than 5 components (i.e. up to 5 particle-5 hole excitations). Our calculations for the pairing problem have indicated high effectiveness of the polynomial representation of the N-projected BCS-function [12] and this paper is devoted to the adaptation of the polynomial

4

representation to the canonical partition function of normal mesoscopic systems.

The material is arranged as following. In Sec.2 separation of the full configuration space into two parts, inside and outside the Fermi sphere, is realized to construct the canonical partition function Z_N as a symmetrical polynomial of N-th order. Z_N is expanded in polynomials of lower orders. These series are composed of products of "particle" and "hole" polynomials, the order of which points out how many particles and holes take part in excitations allowed for in Z_N. In Sec.3 these polynomials are employed to one- and two-body density matrices and on this base the canonical expressions for the heat capacity and magnetic susceptibility are compared to the grand canonical ones. Sec.4 collects recurrent relations for polynomials we apply in calculations. Sec.5 shows that in a wide range of temperatures and particle numbers the elaborated method possesses high convergence and can be used for various types of single-electron energy spectra. The conclusion is given in Sec.6. Algebraic details for the equal level spacing model and the exact canonical partition function of the model are considered in Appendix.

2 "Particle" and "hole" symmetric polynomials and the canonical partition function

If a system is composed of a fixed number N of constituent particles and possesses a discrete excitation spectrum the thermodynamic properties of the canonical ensemble (CE) of such systems can be described by using the partition function Z_N

$$Z_N = \sum_\alpha exp\{-\beta E_\alpha(N)\}, \quad \beta = T^{-1} \tag{1}$$

The index α labels energy states of this system $E_\alpha(N)$, $\alpha = 0$ concerns the ground state. The calculation of $E_\alpha(N)$ for many body systems is a complicated problem and in this paper we limit ourselves by the IEM which in many cases is a good start approximation. Then, assuming that a set of single electron energy levels is established for a static mean field governing the electron movement, the values of E_α are readily found in IEM.

The ground state energy $E_\alpha(N)$ is the sum of N single- electron energies up to the Fermi energy (ε_F) and the excited state energies are obtained by addition to E_0 of several single-electron particle energies $\varepsilon_p > \varepsilon_F)$ and by subtraction

of the same amount (as N is fixed) of hole energies $(\varepsilon_h \leq \varepsilon_F)$

$$E_0(N) = \sum_{s=0}^{F} (\varepsilon_s - \lambda), \tag{2}$$

$$E_\alpha(N) \equiv E_{p_1 p_2 \ldots p_k, h_1 h_2 \ldots h_k} = E_0(N) + \varepsilon_{p_1} + \varepsilon_{p_2} + \ldots + \varepsilon_{p_k} - \\ - \varepsilon_{h_1} - \varepsilon_{h_2} - \ldots - \varepsilon_{h_k}. \tag{3}$$

We shall treat λ in Eq. (2) as a chemical potential, however, in contrast to the grand canonical ensemble (GCE) where λ is calculated to allow for the particle number conservation on the average, the choice of λ for CE as a certain level for counting energies is merely a matter of convenience (in our calculations λ is taken as the grand canonical chemical potential at given T). Substituting Eqs. (2,3) into Eq. (1) one can see that the canonical partition function Z_N is a symmetric polynomial in q_s

$$Z_N = [N] = \sum_{\{distr.\}} \prod_{i=1}^{N} (q_s)_i, \quad q_s = exp[-\beta(\varepsilon_s - \lambda)]. \tag{4}$$

The symbol $(\{distr.\}$ in Eq (4) implies that all N-electron distributions over all single electron levels have to be taken into account.

Another way to introduce Z_N as a symmetrical polynomial consists in employing the statistical operator D_N projected onto a fixed particle number N:

$$\hat{D}_N = \frac{1}{Z_N} P_N \prod_s exp\{-\beta(\varepsilon_s - \lambda)a_s^+ a_s\}, \tag{5}$$

$$P_N = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \, exp\{i\varphi(N - \hat{N})\}, \quad \hat{N} = \sum_s a_s^+ a_s.$$

a_s^+, a_s are the creation and annihilation electron operators. The normalization of $\hat{D}_N$, Z_N, is calculated with unrestricted electron basis ($Fock \ space$) $|\rangle$

$$Z_N = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \, e^{i\varphi N} \, Z(\varphi); \tag{6}$$

$$Z(\varphi) = \langle| \prod_s exp\{[-\beta(\varepsilon_s - \lambda) - i\varphi]a_s^+ a_s\} |\rangle = \\ = \prod_s \{1 + exp[-\beta(\varepsilon_s - \lambda) - i\varphi]\}. \tag{7}$$

6

The Fourier series for Z_N in powers of $e^{-i\varphi}$ includes as amplitudes symmetrical polynomials $[n]$ of the same type as in Eq. (4)

$$Z(\varphi) = 1 + \sum_{n=1} [n] e^{-in\varphi}; \tag{8}$$

$$[1] = \sum_s q_s; \quad [2] = \sum_{s<t} q_s q_t; \quad [n] = \sum_{\{distr.\}} \prod_{i=1}^{n} (q_s)_i \tag{9}$$

The projection in Eq. (6) isolates the polynomial with $n = N$ that again leads to Eq. (4).

If integrating in Eq. (6) ($Z(\varphi)$ from Eq. (8)) is replaced by summing over discrete variable $2\pi l/L$ as was suggested in Ref. [7]

$$\frac{1}{2\pi} \int_0^{2\pi} d\varphi e^{i\varphi(N-n)} \rightarrow \frac{1}{L} \sum_{l=0}^{L-1} e^{i2\pi l(N-n)/L} =$$

$$= \frac{1}{L} \left[1 - e^{-L\varepsilon} \right] \left\{ 1 - e^{i2\pi l(N-n)/L-\varepsilon} \right\} |_{\varepsilon \to 0} =$$

$$= \begin{cases} 1, \ |N-n| = kL; \quad k = 0, 1, \dots \\ 0, \ |N-n| = kL + \nu; \quad l \leq \nu \leq L - 1, \end{cases} \tag{10}$$

then the number projection does not eliminate completely components in the grand canonical Z which correspond to $n \neq N$. However the more is L the larger is the difference between N and such n's (not less than L).

The expectation values of the one- or two body density matrices can be also expressed by means of polynomials

$$\hat{n}_s = a_s^+ a_s,$$

$$n_s = \langle | \ \hat{n}_s D_N \ | \rangle = q_s \frac{[N-1]_s}{[N]}, \tag{11}$$

$$n_{st} = \langle | \ \hat{n}_s \hat{n}_t D_N \ | \rangle = q_s q_t \frac{[N-2]_{s,t}}{[N]}, \quad s \neq t. \tag{12}$$

If state s is degenerated and can be occupied by several electrons, in polynomials there appear powers of the corresponding amplitude q_s. For such cases we introduce n_{ss}:

$$n_{ss} = \langle | \ \hat{n}_s \hat{n}_t D_N \ | \rangle |_{\varepsilon_t = \varepsilon_s} = q_s^2 \frac{[N-2]_{s,s}}{[N]}. \tag{13}$$

Henceforth the notation $[N]_{a,b...}$ implies the exception of single electron states $a, b ...$ out of the full set of states over which n particles are distributed.

For comparison we write out here the GCE results for the same quantities:

$$Z(GCE) = \prod_s (1 + q_s) = 1 + \sum_{n=1} [n].$$ (14)

The maximum n in Eq. (14) is determined by the amount of the single electron states under consideration.

$$\langle | \; \hat{n}_s D(GCE) \; | \rangle = f_s = 1/(1 + q_s^{-1}),$$ (15)
$$\langle | \; \hat{n}_s \hat{n}_t d(GCE) \; | \rangle = f_s f_t, \quad s \neq t,$$ (16)

f_s is the Fermi occupation numbers.

Eq. (12) shows that for the canonical ensemble the two-body density matrix n_{st} is not reduced to a product of two one-body ones $n_s n_t$ as it takes place in GCE, Eq. (16). Thereby the canonical description allows for correlations in electron movement in spite of the starting assumption of the IEM.

The method we are about to develop here for computations of polynomials entering into Eqs. (4), (11)-(13) takes advantage of the general property of symmetrical polynomials: each polynomial given in a space of variables q_s can be represented as a decomposition of polynomials of the same and lower orders defined in subspaces of smaller dimensions. That can be viewed as a consequence of the Clebsch-Gordan decomposition applied to the basic vectors of the symmetric group irreducible representations. If the original space C spans a set of single electron states which can be divided into two subsets $(C = A \oplus B)$ in accordance with energy or any other quantum numbers then an initial polynomial $[n]^{(C)}$ can be represented as following

$$[n]^{(C)} = \sum_{\nu=0}^{n} [n - \nu]^{(A)} [\nu]^{(B)}; \quad [0]^{(A)} = [0]^{(B)} = 1.$$ (17)

Superscripts in this equation denote the spaces in which polynomials are defined. The order of each polynomial $[n - \nu]^{(A)}$ or $[\nu]^{(B)}$ in Eq. (17) cannot exceed the dimension of space A or B respectively.

The first realization of this decomposition is dividing the whole single electron energy space into two parts: below and above the Fermi level (F) that drastically simplifies the calculation of the polynomials and hence, as it will be shown in Sec.5, enables the canonical approach to be employed in a wide range of temperatures and particle numbers.

To implement such dividing we have to explicitly allow for possible degeneracy of electron states and in particular the degeneracy of the Fermi level, d_F. If $d_F > 1$ the occupation rate of F dictates three ways to factorize of $[N]$

$$Z_N = [N] = Z^{(0)} \widetilde{Z}_N \tag{18}$$

The first case corresponds to the completely filled Fermi level at $T = 0$ ($n_F = d_F$, n_F is the particle number on F-level). Then the first factor on the right side of Eq. (18) is the polynomial $[N]^{(A)}$ where space A of the dimension N involves all states below and including F. Therefore this polynomial consists of only one term and is the product of all q_s with s running states $\leq F$. Factoring out this term in Eq. (18) leads to a series in symmetrical polynomials:

$$Z^{(0)} = \prod_{s \leq F} (q_s)^{d_s} = exp\left[-\beta E_0(N)\right], \quad \widetilde{Z}_N = \sum_{n=0}^{N} \overline{[n]}[n], \tag{19}$$

$$\overline{[0]} = [0] = 1,$$

d_s is the degeneracy of state s (d_s is equal to the maximum electron number on this level); $[n]$ and $\overline{[n]}$ are n-th order polynomials, the former is a "particle" polynomial defined in variables $q_s = exp\left[\beta(\lambda - \varepsilon_s)\right] = f_s/(1 - f_s)$, $\varepsilon_s > \varepsilon_F$ while the latter is a "hole" polynomial in $q_t^{-1} = exp\left[\beta(\varepsilon_t - \lambda)\right] = (1 - f_t)/f_t$, $\varepsilon_t \leq \varepsilon_F$, f_s is determined in Eq. (15). Thus, λ being chosen between F and $F + 1$ (the level just above F), both $[n]$ and $\overline{[n]}$ are functions of quantities which are < 1. This choice of λ and exponential energy damping of variables q_s and q_t^{-1} provide the prompt convergence of the series in Eq. (19) especially at small temperatures.

The second case is $n_F \leq d_f/2$ at $T = 0$. Now the factors $Z^{(0)}$ and $\widetilde{Z}_N$ are

$$Z^{(0)} = \prod_{s}^{F-1} (q_s)^{d_s}; \quad \widetilde{Z}_N = \sum_{n=0}^{N-n_F} \overline{[n]}[n_F + n], \tag{20}$$

$F - 1$ is the topmost state just below F.

The third case is $d_F/2 < n_F < d_F$ at $T = 0$, then

$$Z^{(0)} = \prod_{t}^{F} (q_t)^{d_t}; \quad \widetilde{Z}_N = \sum_{n=0}^{N} \overline{[d_F - n_F + n]}[n]. \tag{21}$$

9

3 Canonical magnetic susceptibility and heat capacity

The polynomials $[n]$, $[\bar{n}]$ and those with omitted states determine one- and two-body density matrices (Eqs. (11-13)). Their explicit form for the $n_F = d_F$ case is following ($\tilde{Z}_N$ is defined by Eq. (19)):

$$
n_s =
\begin{cases}
1 - (q_s^{-1}/\tilde{Z}_N) \sum_{n=1}^{N} [n]\overline{[n-1]}_s, & \text{if } s \le F \\
(q_s/\tilde{Z}_N) \sum_{n=1}^{N} [n-1]_s\overline{[n]}, & \text{if } s > F;
\end{cases}
\tag{22}
$$

$$
n_{st} = \frac{q_t n_s - q_s n_t}{q_t - q_s} \qquad s \ne t;
\tag{23}
$$

$$
n_{ss} =
\begin{cases}
1 - (2q_s^{-1}/\tilde{Z}_N) \sum_{n=1}^{N} [n]\overline{[n-1]}_s + \\
\qquad + (q_s^{-2}/\tilde{Z}_N) \sum_{n=2}^{N} [n]\overline{[n-2]}_{ss}, & \text{if } s \le F \\
(q_s^2/\tilde{Z}_N) \sum_{n=2}^{N} [n-2]_{ss}\overline{[n]}, & \text{if } s > F.
\end{cases}
\tag{24}
$$

These density matrices and analogous ones that correspond to Eqs. (20),(21) determine χ_{can} and C_{can}:

$$
\chi_{\text{can}} = \chi_{\text{can}}^{(P)} + \chi_{\text{can}}^{(D)},
\tag{25}
$$

Superscripts P and D mean the paramagnetic and diamagnetic parts of χ.

$$
\chi_{\text{can}}^{(P)} = \frac{\mu_B^2 \beta}{V} \left[\sum_s d_s (\frac{\partial \varepsilon_s}{\partial \omega})^2 n_s (1 - n_s) \right.
$$
$$
+ \sum_s d_s (d_s - 1)(\frac{\partial \varepsilon_s}{\partial \omega})^2 (n_{ss} - n_s^2)
$$
$$
\left. + 2 \sum_{s>t} d_s d_t (\frac{\partial \varepsilon_s}{\partial \omega}) (\frac{\partial \varepsilon_t}{\partial \omega})(n_{st} - n_s n_t) \right],
\tag{26}
$$

$$
\chi_{\text{can}}^{(D)} = -\frac{\mu_B^2}{V} \sum_s d_s \frac{\partial^2 \varepsilon_s}{\partial \omega^2} n_s,
\tag{27}
$$

$$
C_{\text{can}}/k_B = \beta^2 \left[\sum_s d_s (\varepsilon_s - \lambda)^2 n_s (1 - n_s) \right.
$$
$$
+ \sum_s d_s (d_s - 1)(\varepsilon_s - \lambda)^2 (n_{ss} - n_s^2)
$$
$$
\left. + 2 \sum_{s>t} d_s d_t (\varepsilon_s - \lambda)(\varepsilon_t - \lambda)(n_{st} - n_s n_t) \right]
\tag{28}
$$

10

The correlations caused by the particle number conservation formally reveal themselves in the appearance two in Eqs. (26,28) terms containing two-body density matrices (n_{st} and n_{ss}). Besides, due to the correlations, i.e. due to the dependence of the occupation probability of a level on the occupation of the other levels, the Fermi occupation numbers f_s differ from the canonical ones n_s. The grand canonical χ_{grand} and C_{grand} can be obtained from Eqs. (26,28) by replacing n_s by f_s and removing terms proportional to $(n_{st} - n_s n_t)$ and $(n_{ss} - n_s^2)$. Both these factors now vanish since in the absence of the correlations in the grand canonical ensemble two-body matrices are factorized: $(n_{st} = n_s n_t)$ and $(n_{ss} = n_s^2)$.

$$\chi_{\mathrm{grand}} = \chi_{\mathrm{grand}}^{(P)} + \chi_{\mathrm{grand}}^{(D)}, \tag{29}$$

$$\chi_{\mathrm{grand}}^{(P)} = \frac{\mu_B}{V} \beta \sum_s d_s \left(\frac{\partial \varepsilon_s}{\partial \omega} \right)^2 f_s (1 - f_s), \tag{30}$$

$$\chi_{\mathrm{grand}}^{(D)} = -\frac{\mu_B}{V} \sum_s d_s \frac{\partial^2 \varepsilon_s}{\partial \omega^2} f_s,, \tag{31}$$

$$C_{\mathrm{grand}}/k_B = \beta^2 \sum_s d_s (\varepsilon_s - \lambda) f_s (1 - f_s)(\varepsilon_s - \lambda - \beta \frac{\partial \lambda}{\partial \beta}), \tag{32}$$

$$\frac{\partial \lambda}{\partial \beta} = \frac{\sum d_s (\varepsilon_s - \lambda) f_s (1 - f_s)}{\beta \sum d_s f_s (1 - f_s)} \tag{33}$$

Eq. (32) for C_{grand} is written at the condition that the average value of N is conserved. In this case the chemical potential is subject to temperature variations, term in Eq. (32) $\beta \partial \lambda / \partial \beta$. This term is absent if measurements are performed at a constant λ. An analogous term in the susceptibility is dropped, since it is vanishingly small.

4   Calculations of the polynomials

Polynomials entering into $\widetilde{Z_N}$, χ_{can} and C_{can} can be expressed through q_s and q_t^{-1} with help of recurrent procedure based on Eq. (17). If in this equation the partition $C = A \oplus B$ is such that space B consists of only one state s then $[\nu]^B = \delta_{\nu.1} q_s + \delta_{\nu.0}$ and polynomial $[n - \nu]^{(A)}$ in space A is in fact $[n - \nu]_s$ since it is defined in the whole space C with state s omitted. Eq. (17) can be therefore rewritten as

$$[n] = [n - 1]_s q_s + [n]_s. \tag{34}$$

11

The sum rule gives the second equation for successive calculations of polynomials:

$$\frac{1}{n}\sum_s [n-1]_s d_s q_s = [n].\tag{35}$$

The meaning of Eq. (35) is illustrated by its application to Eq.(10)

$$\sum_s [N-1]_s d_s q_s = [N]\langle| \hat{N} D_N |\rangle = [N] \cdot N.\tag{36}$$

Here s enumerate all single electron states.

The lowest order polynomials being found straightforwardly

$$[0] = [0]_t = 1; \quad [1] = \sum_s d_s q_s,\tag{37}$$

higher order ones can be determined by using Eq. (34), that gives the well-known Newton identity (35)

$$[n] = \frac{1}{n}\sum_{\nu=1}^n [n-\nu]a_\nu(-1)^{\nu-1},\tag{38}$$

$$a_\nu = \sum_s d_s q_s{}^\nu.\tag{39}$$

Eq. (38) can be used to express $[n]$ only through a_ν, Eq. (39), such formula is given in textbooks on algebra, but it is not so convenient for calculations as Eq. (38).

$$[n]_t = \sum_{\nu=0}^n [n-\nu]q_t^\nu(-1)^\nu.\tag{40}$$

If $q_s \neq q_t$ for states s and t then

$$[n]_{st} = \sum_{\nu=0}^n [n-\nu](-1)^\nu \sum_{\mu=0}^\nu q_s^{\nu-\mu}q_t^\mu$$
$$= (q_t[n]_t - q_s[n]_s)/(q_t - q_s)\tag{41}$$
$$= ([n+1]_t - [n+1]_s)/(q_s - q_t).\tag{42}$$

If state s is degenerated $(d_s > 1)$ then it is possible to define $[n]_{ss}$, Eq. (13), as following

$$[n]_{ss} = \sum_{\nu=0}^{n} [n-\nu](-1)^{\nu} q_s^{\nu} (\nu+1) \qquad (43)$$

or by using recurrent relations

$$[0]_{ss} = 1, \quad [n]_{ss} = [n]_s - q_s[n-1]_{ss} \qquad (44)$$

Eqs. (38), (40-43) are sums of sign-changing terms. Instead of them one can use sums with positive terms

$$[n]^{(C)} = \sum_{\mu_1+\mu_1+\ldots+\mu_n=n} [\mu_1]^{(S_1)} \cdot [\mu_2]^{(S_2)} \cdot \ldots \cdot [\mu_n]^{(S_n)}. \qquad (45)$$

that can be obtained from Eq. (17). Superscripts in Eq. (45) assume that $C = S_1 \oplus S_2 \oplus \ldots \oplus S_n$ where each subspace S_i embraces $d(S_i)$ single electron states, therefore $\mu_i \leq d(S_i)$. If these states are degenerated, any polynomial in Eq. (45) is calculated analytically

$$[\mu]^{(S)} = C_{\mu}^{d(S)} exp\{-\beta\mu(\varepsilon_s - \lambda)\}, \quad C_{\mu}^{d(S)} = \begin{pmatrix} d(S) \\ \mu \end{pmatrix}. \qquad (46)$$

C_B^A is a binomial coefficient. Eqs. (45), (46) are appropriate to calculate the derivatives of $[n]$ with respect to q_s

$$\frac{\partial[n]}{\partial q_s} = d_s[n-1]_s; \quad \frac{\partial^2[n]}{\partial q_s^2} = d_s(d_s-1)[n-2]_{ss}. \qquad (47)$$

If each subspace S_i is nondegenerate, i.e. each $\mu_i = 0$ or 1, Eq. (45) is transformed into the sum over distributions similar to Eq. (4).

When a magnetic field is applied to a system in which spin and orbital momenta are decoupled each electron spin is aligned along or against the field B. That gives rise to the Zeeman splitting of the single electron levels

$$\varepsilon_s = \varepsilon_s(B) \pm \omega, \quad \omega = \mu_B^* \frac{g}{2} B, \qquad (48)$$

μ_B^* is the effective Bohr magneton and g is the effective gyromagnetic ratio. $\varepsilon_s(B)$ incorporates magnetic effects on the spatial electron density. The

spin splitting can be explicitly separated in Z_N by means of dividing the whole space C of single electron states into two subspaces: $C = C^{(+)} \oplus C^{(-)}$, $C^{(+)}$ spans states with positive magnetic spin contributions $+\omega$ to the energy, Eq. (45), $C^{(-)}$ corresponds to $-\omega$. Such partition causes the decomposition of each polynomial:

$$[n] = \sum_{\nu=0}^{\nu_m} [n-\nu]^{(+)} [\nu]^{(-)}; \quad \nu_m = min(n, G). \tag{49}$$

G is the whole amount of single particle levels which were twice degenerate in the absence of the field. Polynomials $[\nu]^{(\pm)}$ include factors $exp[\mp\beta\omega\nu]$ that allows one to reduce Eq. (49) to the form

$$[n] = \exp\{-\beta\omega n\} \sum_{\nu=0}^{n} \exp\{2\beta\omega\nu\}[[n-\nu]][[\nu]] =$$

$$\sum_{\nu=0}^{(n-\xi_n)/2} [2 - (1-\xi_n)\delta_{\nu.0}] \left[\left[\frac{n+\xi_n}{2} + \nu\right]\right] \left[\left[\frac{n-\xi_n}{2} - \nu\right]\right] \times$$

$$\cosh\left[\beta\omega(2\nu + \xi_n\right], \tag{50}$$

$$\xi_n = [1 - (-)^n]/2 \,.$$

The polynomials $[[(n \pm \xi_n)/2 \pm \nu]]$ in Eq. (50) are composed of q_s independent of the spin magnetism: $q_s = \exp\{-\beta[\varepsilon_s(B) - \lambda]\}$, $\varepsilon_s(B)$ is given by Eq. (48). Eq. (50) is employed in Appendix to find Z_N for the equal level spacing model. Eqs. (35 - 50) are written out for "particle" polynomials $[n]$ for which space G stretches from level $(F+1)$ up to the topmost level M. The same equations are applied to "hole" polynomials $\overline{[n]}$ provided variables q_s with $(\varepsilon_s(B) - \lambda) > 0$ are replaced by q_t^{-1} with $(\varepsilon_t(B) - \lambda) < 0$. The level space for $[\bar{n}]$ ranges along all single-particle space beneath and including level F.

5   The potentialities of the polynomial method

As mentioned in Introduction the best temperature regime to reveal the difference between canonical and grand canonical description is $T < \delta_F$. At this condition the convergence of series over n for $\widetilde{Z}_N$, Eqs. (19)-(21), is attained by taking into account as low as a few terms ($n \ll N$). However, in this section we will show that the polynomial method can be applied in a wide temperature range since these series possess the absolute convergence. Moreover, even for such high temperature as $T \sim 50\delta_F$ real values of n do not surpass $n_{\max} \sim 100$ for $N \sim 10^5$, i.e. $n_{\max}$ is far smaller than N, and the most part of series for $\widetilde{Z}_N$, which in the general case stretch to N, does not contribute to $\widetilde{Z}_N$.

14

Firstly we shall accomplish estimates of the convergence analytically and exploit for this purpose the equal level spacing model that is reasonable approximation to a real system at high temperatures $T > \delta_F$ when details of possible shell structure are averaged out. To avoid the double degeneration of levels we dispose the system in a weak magnetic field B to actualize the Zeeman splitting, Eq. (48). If $\omega = \Delta/4$ ($g_s = 2$) the levels are equidistantly placed as before with the level spacing $\Delta/2$. Here and in Appendix Δ is used for the level spacing at $B = 0$. In this case the polynomials entering into $\widetilde{Z}_N$

$$\widetilde{Z}_N = \sum_{n=0}^{N} z(n), \quad z(n) = [n]\overline{[n]}, \tag{51}$$

are defined in a space of "particle" (q_s) and "hole" (q_t^{-1}) variables, Eq. (4), reduced to powers of q (here we put $\lambda = \varepsilon_F$):

$$q = \exp(-1/t), \quad t = 2T/\Delta \tag{52}$$
$$q_s = \exp\left[-\beta(\varepsilon_{F+s} - \varepsilon_F)\right] = q^s \tag{53}$$
$$q_t^{-1} = \exp\left[-\beta(\varepsilon_F - \varepsilon_{F-t})\right] = q^t \tag{54}$$

As shown in Appendix polynomials in such variables can be found analytically, Eq.(A3). If $M > N \gg 1$ these expressions are simplified

$$\overline{[n]} = q^{n(n-1)/2} \prod_{\nu=1}^{n} (1 - q^\nu)^{-1}, \quad [n] = q^n \overline{[n]}. \tag{55}$$

At small T when $t \ll 1$ the series for $\widetilde{Z}_N$ is exhausted by few first terms since $q \ll 1$. However the convergence falls if T increases giving rise to $q \sim 1$. At such temperatures the polynomials $[n]$ are increased with n up to some n_0 after which they begin decreasing. An estimation of n_0 is obtained from the condition:

$$\frac{z(n_0 - 1)}{z(n_0)} < 1, \quad \frac{z(n_0 + 1)}{z(n_0)} < 1, \tag{56}$$

Substituting Eq. (55) into Eq. (56) gives

$$n_0 \simeq t \ln(1 + \exp\{1/2t\}) \simeq 0.7t. \tag{57}$$

Thus n_0 increases with t and practically does not depend on N if $n_0 \ll N$. The upper limit of summation, $n_{\max}$, can be found from the condition

$$\frac{z(n_{\max} + 1)}{z(n_{\max})} < 0.1$$

This equation yields $n_{\max} \sim 2n_0$ that is demonstrated by Fig. 1 where the results of the exact calculations of $\widetilde{Z}_N$ for the equal level spacing model are given. It displays the ratios of $\widetilde{Z}_N$ calculated with few terms of the full sum in Eq. (51) to the exact value of $\widetilde{Z}_N$. At a fixed temperature the bend points for $N = 10^2 \div 10^5$ practically coincide. These points correspond to n_0 and the saturation sets in even earlier than at $2n_0$.

As shown in Fig. 2 the values of n_0 at a fixed reduced temperature (T/δ_F) depends on the type of the electron confinement. The energy single-electron spectra of the equal level spacing model and that of the anysotropic oscillator are similar. Therefore similar is the convergence of the corresponding $\widetilde{Z}_N$-series. For a spherical cavity the spectrum reveals shell gaps. In consequence the convergence turns out to be somewhat higher.

At high temperatures $q \simeq 1 - 1/t$ and $1 - q^n \simeq n/t$, therefore the n-dependence of any term $z(n)$ in Eq. (51) at $n \gg 1$ can be obtained from Eq. (55)

$$z(n) \mid_{n \gg 1} \sim \frac{(t)^{2n}}{(n!)^2}, \tag{58}$$

that proves the absolute convergence of $\widetilde{Z}_N$-series.

Asymptotic values of $\widetilde{Z}_N$ at high temperatures can be found if summing over single-particle states is replaced by integrating with that part of the level density $\rho(\varepsilon)$ which is monotonously varying with energy ε. At such T the fluctuation part of $\rho(\varepsilon)$ (shell correction) practically brings no contribution. Along with this approximation two other conditions are employed: $T \ll \varepsilon_F$ and $N \gg 1$.

Z_N in IEM defined as an integral, Eqs.(6),(7), can be represented as following

$$Z_N = \exp\{-\beta(E_0 - \lambda N)\} \frac{1}{2\pi} \int_0^{2\pi} d\varphi \exp(A + B) \tag{59}$$

$$A = \sum_{s \leq F} \ln\{1 + \exp[\beta(\varepsilon_s - \lambda) + i\varphi]\} \rightarrow$$

$$\rightarrow \beta^{-1} \int_0^\lambda \rho(\lambda - y\beta^{-1}) \ln[1 + \exp(-y - i\varphi)] \, dy \tag{60}$$

$$B = \sum_{t > F} \ln\{1 + \exp[-\beta(\varepsilon_t - \lambda) + i\varphi]\} \rightarrow$$

$$\rightarrow \beta^{-1} \int_0^\infty \rho(\lambda - y\beta^{-1}) \ln[1 + \exp(-y - i\varphi)] \, dy \tag{61}$$

16

For $N \gg 1$ the upper limit λ in Eq. (60) is extended to ∞. Then taking into account only first term (independent of β) in the expansion of functions $\rho(\lambda \pm y\beta^{-1})$ one arrives at

$$A + B = \rho(\lambda)\beta^{-1} \int_0^\infty \ln\left(1 + 2\cos\varphi e^{-y} + e^{-2y}\right) dy =$$

$$= \frac{\rho(\lambda)\beta^{-1}}{2}(\pi^2 - \varphi^2), \quad \varphi \leq \pi, \tag{62}$$

Thus Z_N gains the form

$$Z_N = \exp\left\{-\beta(E_0 - \lambda N) + \pi^2\rho(\lambda)/6\beta\right\}\xi,$$

$$\xi = \frac{1}{\pi}\int_0^\pi d\varphi \exp\left[-\rho(\lambda)\beta^{-1}\varphi^2/2\right] \tag{63}$$

As $\rho(\lambda)\beta^{-1}$ is supposed to be $\gg 1$ the upper limit in the integral in Eq. (63) can be taken as ∞:

$$Z_N = \left(\frac{\beta}{2\pi\rho(\lambda)}\right)^{1/2}\exp\left[-\beta(E_0 - \lambda N) + \pi^2\rho(\lambda)/6\beta\right] \tag{64}$$

The value of Z_{grand} is found from Eq. (63) if $\xi = 1$

$$Z_{\text{grand}} = \exp\left[-\beta(E_0 - \lambda N) + \pi^2\rho(\lambda)/6\beta\right]. \tag{65}$$

In Eq. (65) λ is regarded as a function of T defined by the particle number conservation.

Now one can see the difference between C_{can} and C_{grand}

$$C_{\text{can}} = k_B\beta^2\frac{\partial^2 \ln Z_N}{\partial\beta^2} = k_B^2 T\rho(\lambda)\pi^2/3 - k_B/2; \tag{66}$$

$$C_{\text{grand}} = k_B\beta^2\frac{\partial U}{\partial\beta};$$

$$U = -\frac{\partial \ln Z_{\text{grand}}}{\partial\beta}\Big|_{\lambda=const} + \lambda\beta^{-1}\frac{\partial \ln Z_{\text{grand}}}{\partial\lambda},$$

$$C_{\text{grand}} = k_B^2 T\rho(\lambda)\pi^2/3. \tag{67}$$

17

In Eq. (67) the condition $T/\varepsilon_F \ll 1$ and the relation

$$\rho(\lambda)\partial\lambda/\partial\beta \simeq \beta^{-3}(\partial\rho/\partial\lambda)\pi^2/3$$

are employed. Thus the difference between C_{can} and C_{grand} is the same as it was found in Ref. [2] for the equal level spacing model. Eqs. (66,67) show that the same difference exists for any level density.

As shown in Appendix the exact canonical partition function for the equal level spacing model turns out to be much more complicated than the expression given in Ref. [2] in approximation $M > N \gg 1$. However the difference reveals itself mainly at small particle number and $T/\Delta > 1$. This is demonstrated in Figs. (3),(4) where C_{can} is displayed v.s. N and T.

6 Conclusion

We have shown that the canonical partition function Z_N which in general case is a symmetric polynomial of the N-th order (in variables of $\exp\{\beta(\lambda - \varepsilon_s)\}$) can be expanded in polynomials the orders of which range from 0 to N. Such representation of Z_N takes into account that in the independent particle model the full configuration space is naturally divided by the Fermi surface and each excitation in this model is generated by particle-hole pairs the amount of which range from 0 to N as well. Therefore the polynomial expansion of Z_N is a sum over products of particle and hole symmetric polynomials the order of which vary in the same manner as the amount of pairs in the excitation.

In consequence the canonical averages such as the occupation numbers, heat capacity and magnetic susceptibility are expressed via similar sums involving the same polynomials and others defined in narrower spaces (where a part of states is omitted). We have suggested recurrent relations reduced the calculations of n-th order particle (hole) polynomials, corresponding to distributions of n particles (holes) over states above (below) the Fermi level, to first order polynomials.

Though the sum Z_N stretches to N-th order polynomials, its convergence is so high that this version of the exact canonical approach can be employed for mesoscopic systems in a wide range of temperatures and particle numbers. Moreover , as only few first terms bring in a real contribution to canonical averages in the temperature range of several level spacings near the Fermi level, the elaborated method is especially effective for studying structure and size effects in the temperature regime which is most appropriate to this goal.

A   The canonical partition function of the equal spacing model.

In this model each single electron level in the applied magnetic field B gains the Zeeman splitting

$$\varepsilon_s^{\pm} = s\Delta \pm \omega \tag{A.1}$$

Δ is the level spacing, $s = 0, 1, \ldots, M - 1$, where M is the amount of the electron levels, $M > N$. N is the electron number. Thus each polynomial in Eq. (50 is defined in the space of q_s (here we set $\lambda = 0$)

$$q_s = q^s, \quad q = exp(-\beta\Delta), \tag{A.2}$$

that allows a polynomial $[[k]]$ to be calculated analytically

$$[[k]] = q^{k(k-1)/2}Q(M, k), \tag{A.3}$$

$$Q(M, k) = \delta_{k.0} + (1 - \delta_{k.0}) \prod_{\kappa=1}^{k} (1 - q^{M+1-\kappa})/(1 - q^{\kappa})$$

Eq. (A.3) is straightforwardly found for all k at small M and then extended for any M by induction. Substituting Eq. (A.3) into Eq. (50), where n has to be replaced by N, one obtains

$$Z_N = [N] = exp\{-\beta E_0(N)\}\widetilde{Z_N}, \tag{A.4}$$

$$\widetilde{Z_N} = \sum_{\nu=0}^{\frac{[N-\xi_N]}{2}} \{2 - [1 - \xi_N]\delta_{\nu.0}\} q^{\nu(\nu+\xi_N)}$$

$$\times Q(M, \frac{N + \xi_N}{2} + \nu)Q(M, \frac{N - \xi_N}{2} - \nu) \cosh\{\beta(2\nu + \xi_N)\},$$

$$\xi_N = \frac{1 - (-1)^n}{2}.$$

$E_0(N)$ is the ground state energy in this model at $T = B = 0$; $E_0(N) = \Delta[N(N - 2) + \xi_N]/4$.

Eq. (A.4) is the exact partition function. In order to crossover to the expression given in Ref.[2] two approximations have to be done. Firstly the amount of the levels M has to be infinitely large, $M \to \infty$, then

$$Q(M, k) \to Q(\infty, k) = \delta_{k.0} + (1 - \delta_{k.0}) \prod_{\kappa=1}^{k} (1 - q^{\kappa})^{-1}.$$

Secondly the values of $q = exp(-\beta\Delta)$ must be small enough whereas the particle number $N \gg 1$ then the dependence Q on ν in Eq. (A.4) can be dropped

$$Q(\infty, \frac{N \pm \xi_N}{2} \pm \nu) \to \prod_{\kappa=1}^{\infty} (1 - q^{\kappa})^{-1}.$$

References

[1] W. D. Knight, W. A. Heer, and K. Clemenger Solid State Commun. **53** 445 (1985);W. A. Heer, W. D. Knight, W. D. Chou, and M. L. Cohen Solid State Phys. **40** 93 (1987).

[2] R. Denton, B. Mühlschlegel, O. J. Scalpino, Phys. Rev. Lett. **26**, 707 (1971); Phys. Rev. **B7**, 3589 (1973).

[3] N. K. Kuzmenko and V. M. Mikhajlov, Phys. Lett. **A296**, 49 (2002).

[4] M. Brack, O. Genzken and K. Hansen, Z. Phys. **D21**, 65 (1991).

[5] W. P. Halperin Rev. Mod. Phys. **58** 533 (1986).

[6] J. A. A. J. Perenboom, P. Wyder and F. Meier, Phys. Reps. **78**, 173 (1981).

[7] G. H. Lang, C. W. Johnson, S. E. Koonin, and W. E. Ormand, Phys. Rev. **C48**, 1518 (1993).

[8] S. Frauendorf, V. V. Pashkevich, Surface Rev. and Lett. **3**, 241 (1996).

[9] R. Rossignoli, Phys. Rev. **C51**, 1772 (1995).

[10] H.-J. Schmidt and J. Schnack, arXiv: cond-math/0104293 2001; arXiv: cond-math/0209397 2002.

[11] F. Philippe, J. Arnaud, L. Chusseau, arXiv: math-ph/0211029 2002.

[12] N. K. Kuzmenko, V. M. Mikhajlov, Bull. Acad. Sci. USSR, Ser. phys., **37**, 1911 (1973); Sov. J. Part. & Nucl., **20**, 830 (1989); Phys. Rev., **C51**, 2826 (1995).
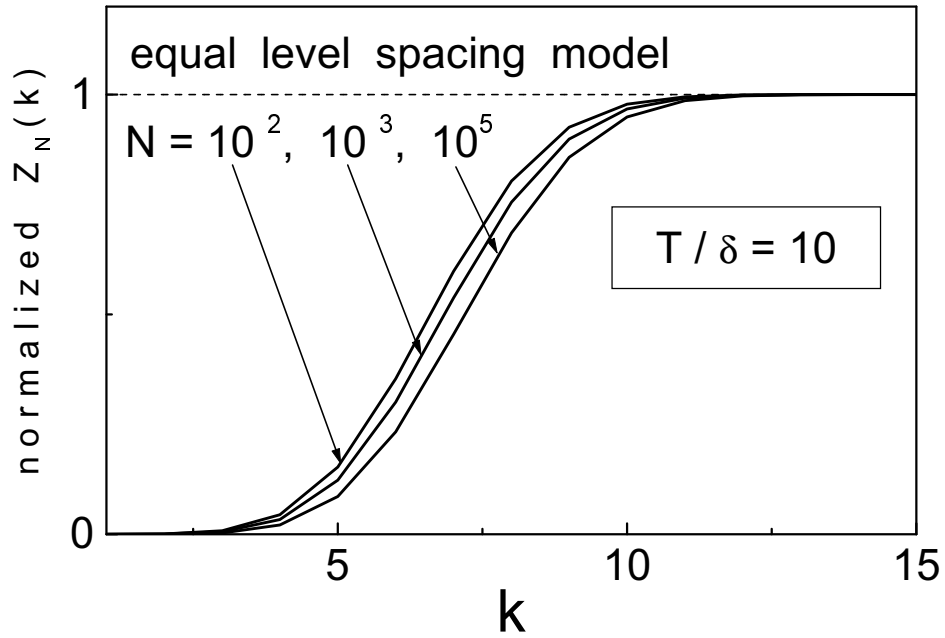
Fig. 1. The rate of the convergence of series in symmetrical polynomials. Normalized $Z_N(k)$ is $\sum_{n=0}^{k}[n][\bar{n}]/\sum_{n=0}^{N}[n][\bar{n}]$.
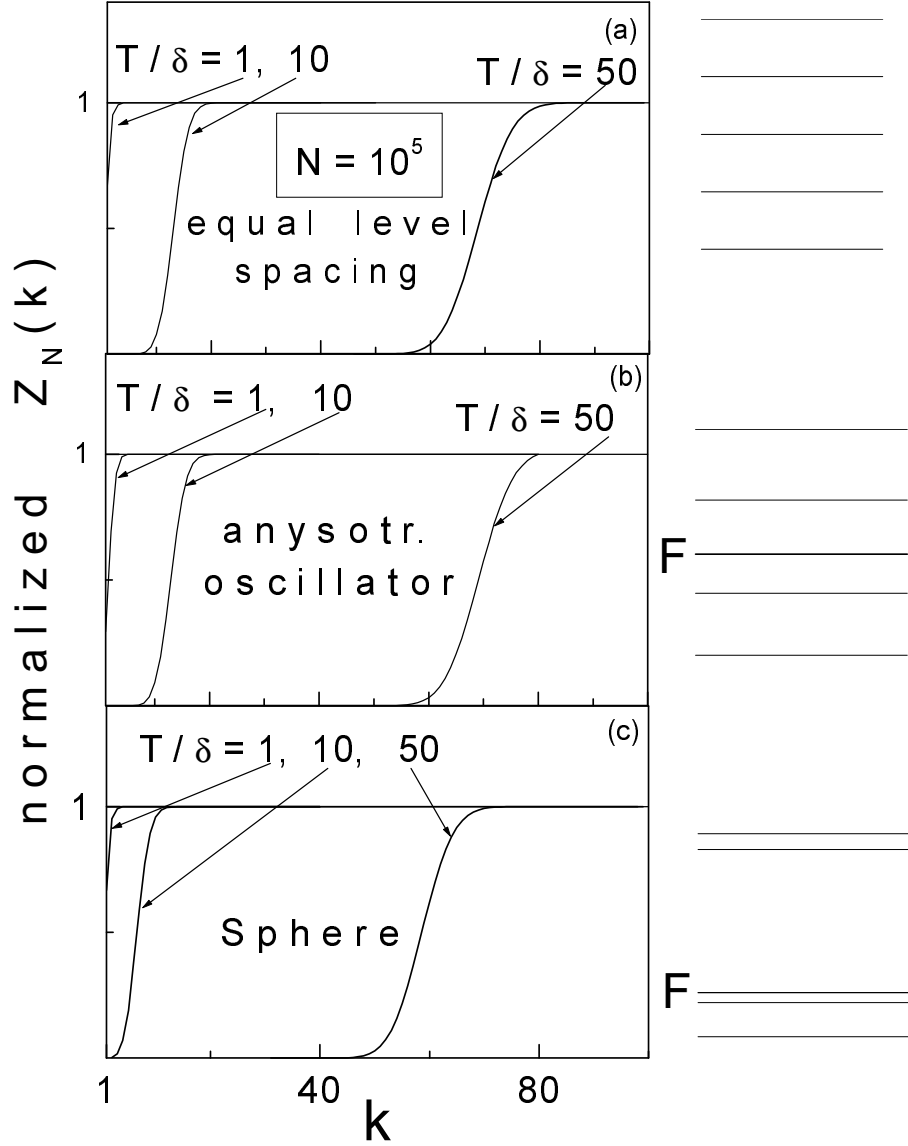
Fig. 2. Influence of the temperature on the convergence of series Z_N for different model spaces. $Z_N(k)$ is defined in the capture to Fig.1. δ is the mean level spacing near the Fermi level. The right panel shows fragments the single-electron spectra near the Fermi level for these model spaces:(a) the equal level spacing; (b) an anysotropic oscillator potential with frequencies $\omega_x/\omega_y = 1.33$, $\omega_x/\omega_z = 1.55$; (c) a spherical cavity with $R = r_0 N^{1/3}$.
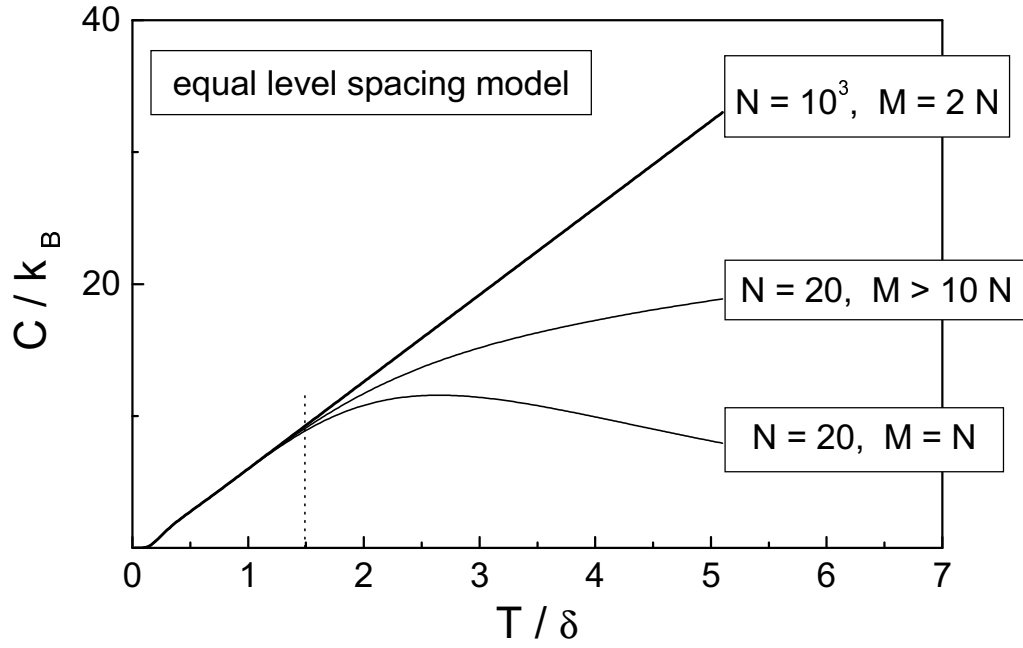
Fig. 3. The canonical heat capacity vs temperature. The bold curve represents the results of Ref. [2] and coincide with the exact canonical results if $N \geq 10^3$. For smaller N the high temperature ($T > 1.5\delta$) behavior of C_{can} (the curve for $N = 20$, $M \geq 10N$, M is the number of spin degenerate single-electron levels) differs from predictions of Ref. [2]. The curve for $N = 20$, $N = M$ shows that high temperature behavior of C in small electron ensembles depends on M if $M < 10N$.
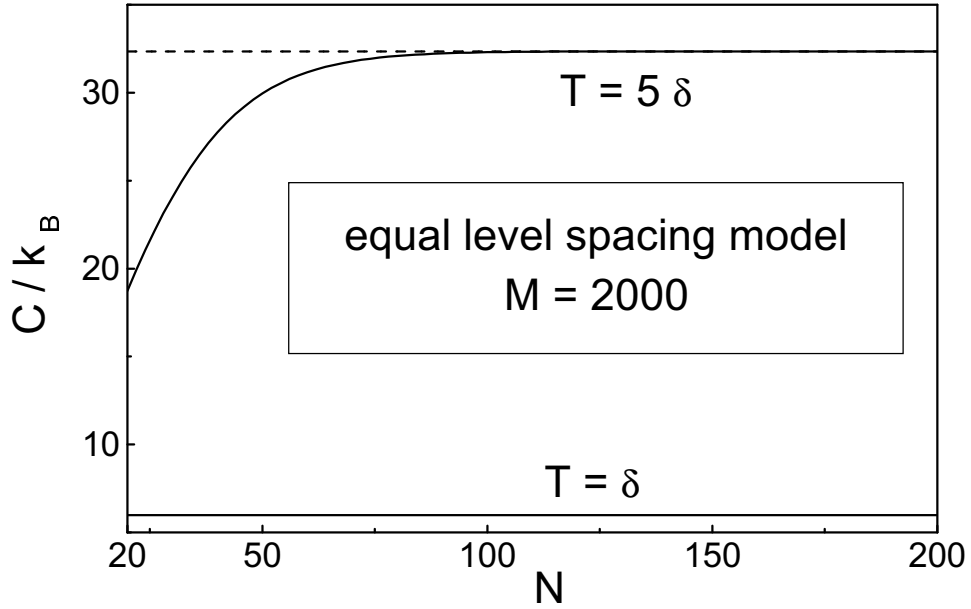
Fig. 4. The canonical electronic heat capacity vs the particle number in the equal level spacing model (δ is the level spacing). Solid lines represent the results obtained by our method. The dashed line represents the result of Ref. [2]. At $T = \delta$ the exact canonical results coincide with the results of Ref. [2].